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(54) Extinguishing Medium and Process for Its Production

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EXTINGUISHING MEDIUM AND PROCESS FOR ITS PRODUCTION

ABSTRACT OF THE DISCLOSURE

An extinguishing medium is proposed, which is useable both as a dry extinguishing medium and as an extinguishing medium additive in water. The main constituents of the extinguishing medium are on the one hand pulverulent, hydrogel-forming polymers and on the other substances with a large surface structure and/or capillary and/or fibrous structure. These main constituents of the extinguishing medium are homogeneously mixed to form a free-flowing medium.

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EXTINGUISHING MEDIUM AND PROCESS FOR ITS PRODUCTION

BACKGROUND OF THE INVENTION

The invention relates to an extinguishing medium for use as a dry or powder extinguishing medium or as an extinguishing medium additive in water and also covers a process for the production of the extinguishing medium.

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The most frequently used extinguishing medium is water, which has a number of advantages for this purpose. It is firstly necessary to stress its cooling action, i.e. its heat absorbing capacity. 2257 KJ (539 kcal) are required in order to completely evaporate one litre of water. During the extinguishing action the water removes the heat from the flammable material to below the ignition temperature, so that the fire is extinguished. Water also has a mechanical extinguishing action, because it passes from a jet pipe onto the flammable mass, divides up the latter and consequently aids the extinguishing action. In addition, during extinguishing with water steam is formed, because at temperatures of approximately 100°C and higher the water is completely evaporated. Thus, one litre of water produces 1700 litres of steam, which at the fire point displaces the oxygen necessary for burning. Finally, with the aid of simple mechanisms such as pumps, pipes, etc. water can easily be conveyed to the fire point, if a hydrant or water reservoir is reasonably close to the centre of the fire.

However, besides these undisputed advantages, during extinguishing water also has a number of disadvantages. Thus, water does not remain sufficiently long at the centre of the fire, because it rapidly flows away. It is therefore necessary to use considerable quantities of water

over long periods of time in order to successfully fight the fire. Outside well inhabited areas, e.g. in forests, cut-of-town settlements, mountain regions in Southern latitudes, etc. water is rarely available in adequate quantities. During the flowing away of extinguishing water considerable amounts of pollutants and contaminants can be washed out, e.g. when fighting fires in chemical A re-use of the extinguishing water is installations. rarely possible, because due to its content of contaminants the water is mixed with aggressive media. In addition, with normal fire brigade centrifugal pumps it is not possible to deliver in a satisfactory manner extinguishing water at temperatures equal to or higher than approximately 40ºC.

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When extinguishing water is used there is a fear of the consequential damage, which further increases the fire damage. In the case of fires in rooms or dwellings it is always necessary to expect water damage to furniture, walls, ceilings, electrical appliances, etc. With fires in industrial or agricultural storage buildings regularly large amounts of stored products are rendered unusable by the extinguishing water. In addition, the stored products contaminate the extinguishing water and increase the environmental damage caused by the draining off water. For forest fires there is generally insufficient water available, because it must be brought in over considerable distances, e.g. by means of hose lines which firstly have to be laid or by means of water containers which have to be brought in, but which only have a limited capacity, as is e.g. the case for fire extinguishing tankers and helicopters and aircraft used for fire fighting purposes.

There have been numerous attempts to improve the extinguishing technology based on water. Firstly fire

planned use of the water. Use is made of numerous different jet pipes, such as e.g. multi-purpose jet pipes, mist or fog nozzles, etc. Use is also made of high-speed pumps with discharge pressures over 100 bar. Water use is also optimized by sprinkler systems and flooding systems with special water nozzles. It is also known to use water additives such as foaming agents, flow accelerators and wetting agents. In addition, polymeric superabsorbers have already been added to the extinguishing water.

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These known methods for optimizing the use of water during extinguishing operations suffer from considerable disadvantages and are unable to remove the aforementioned disadvantages of water as an extinguishing medium.

Thus, water mixed with a foaming agent, such as is used in flammable liquids for forming a barrier layer between the burning liquid and the oxygen, generally has no cooling action. As the foaming agent is admixed in considerable quantities of approximately 4% by weight and it is harmful to the water, the use of foaming agents is generally prejudicial to the environment.

25 Flow accelerators only have one effect, namely that of increasing the range of the water jet, by reducing the frictional resistance in pipes, lines and hoses. The extinguishing action itself is not improved by flow accelerators. As far as is known, flow accelerators have only been used by fire brigades for testing purposes.

The field of use for wetting agents is imited, e.g. to fires in coal heaps, in order to reduce the surface tension of the water and therefore to enable the water to penetrate the lower layers of the heaps.

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Tests with polymeric superabsorbers as extinguishing water additives have also failed to provide usable results or have completely failed. Reference is firstly made in this connection to the agglomeration in the pipes and after passing out of the latter and therefore a considerable failure probability during use, which can even lead to inoperability. Agalomeration also reduces the range to a significant extent compared with pure water. In addition, superabsorbers due to the gel formation with water lead to a delayed swelling of the overall quantity of the superabsorber used, which on the one hand encourages agglomeration and on the other leads to a significant As superabsorbers are not soluble in additional use. water, a sticking and unusability of the fittings must be Due to the non-uniform swelling behaviour expected. delivery is not possible with normal fire extinguishing centrifugal pumps. This method has consequently not gone beyond the experimental stage.

SUMMARY OF THE INVENTION

An object of the invention is to provide an extinguishing medium, which can be used both as a dry extinguishing medium and as an extinguishing medium additive in water and which does not have or does not significantly have the disadvantages of known extinguishing media or extinguishing medium additives. Processes suitable for producing the extinguishing medium are also proposed.

- According to the present invention there is provided an extinguishing medium for use both as a dry extinguishing medium and as an extinguishing medium additive for addition to water comprising the following constituents:
- a) at least one pulverulent, hydrogel-forming polymer,
 and

b) at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure,

which are homogeneously mixed to form a free-flowing medium.

The invention also provides a process for producing an extinguishing medium for use both as a dry extinguishing medium and as an extinguishing medium additive for addition to water, comprising the following main constituents:

- a) at least one pulverulent superabsorber, and
- b) at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure,

which process comprises mixing the said at least one constituent substance optionally with at least one additive and simultaneously or subsequently admixing therewith the superabsorber which has been mechanically comminuted and dried and thereby rendered free-flowing.

In a first variation the process comprises mixing the said at least one constituent substance with the mechanically comminuted, aqueous superabsorber raw product which has been obtained by gel polymerization, prior to the drying thereof, and kneading the mixture, followed by drying, grinding and then optionally admixing at least one further constituent.

In a second variation the process comprises mixing the said at least one constituent substance with a monomer solution of the superabsorber, polymerizing the mixture obtained according to known gel polymerization techniques, drying

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and grinding the resulting product and then optionally admixing at least one further constituent.

The invention also provides the use of the claimed extinguishing media in various ways.

DESCRIPTION OF PREFERRED EMBODIMENTS

The preferred extinguisting media, processes for making them and uses are as set out in the claims hereof.

In the extinguishing medium composition according to the invention the pulverulest, hydrogel-forming polymers known under the name "superabsorbers" mainly ensure the water transportation. The invention makes use of the enormous swelling capacity of such superabsorbers. The water consumption remains relatively low, because the bound water cannot flow away and comsequently remains to a significant extent at the centre of the fire and can exert over longer periods its already described advantageous effects. This In addition, leads to reduced water damage. extinguishing medium forms a salt-like, dry crust, which makes re-ignition more difficult, on the extinguished surfaces and the surfaces to be protected against ignition. The crust can still have a certain swelling capacity, so that water or precipitation striking it can bring about a re-activation of the extinguishing medium.

Substances with a large surface structure and/or capillary and/or fibrous structure are incorporated between the superabsorber granules after mixing with the superabsorber and are fixed there optionally by the addition of, for example, a polyglycol, e.g. polyethylene glycol, in an amount of up to 30%, and preferably up to 10%, by weight. Thus, despite the swelling of the superabsorber granules to

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gel particles the water is still rapidly and completely distributed and passes through the capillary or fibrous structures to all the superabsorber granules and make the latter uniformly rapidly swell. This effect speeds up the swelling behaviour of the superabsorber by a multiple and prevents agglomeration. Said substances prevent a sticking of the gel mass following the swelling of the superabsorber, even during prolonged storage or violent vibrations. As an agglutination or sticking is prevented, the wet extinguishing medium can be delivered and distributed without agglomeration. Following application the gel particles can fall apart, which significantly improves the extinguishing medium activity of the water.

If e.g. 1000 litres of water are mixed with 10 kg of extinguishing medium without mechanical aids, then after about 2 to 5 minutes the 1000 litres of water have become a homogeneous, gel-like mass. If this mass is transported to the centre of the fire and poured out by opening extinguishing flaps, said mass is transformed into finely divided gel particles, which form a uniform layer e.g. on trees, shrubs and lawns, no agglomeration occurring. The extinguishing action is excellent. A pump premixing of the extinguishing medium of the present invention is possible without fittings becoming dirty, sticky and unusable, even if the extinguishing process is briefly stopped. mixing of the extinguishing medium additive with water in an admixer or jet pipe can, as a function of the requirements of the extinguishing action, be switched on or off, without there being any risk of the fittings becoming clogged. The appliances can in fact be flushed again with water and are immediately ready for use again. practice, less extinguishing medium is used for a shorte-Naturally there is also less extinguishing time. contaminated extinguishing water.

If the extinguishing medium according to the invention in its use as an extinguishing medium additive in water meets a hot surface, e.g. wood, the water removes the heat from the said surface, so that there is a cooling extinguishing action through the evaporation of the water until the flames are extinguished on dropping below the flash point. In the area where the water has evaporated, formation takes place of the indicated salt-like crust from the extinguishing medium which, in conjunction with at least one fireproofing agent, flame retardant or fire retardant preferably up to 10% by weight, prevents the flowing residues from re-igniting or being rapidly re-ignited by external ignition attempts. Two important physical effects come into action namely on the one hand the cooling action of the water and on the other hand the fireproofing medium acting against re-ignition. The fireproofing medium can be constituted by colloidal solutions of sodium or potassium However, it is also possible to use other silicates. Through the use of commercial flame retardants. fireproofing agents or flame retardants the ignition temperature of the extinguishing medium additive is roughly doubled, namely from approximately 440 to 900°C, without flame formation.

When using the extinguishing medium as a dry extinguishing medium it has been found that the finely divided, pulverulent mixture has an inhibiting action in the flame picture and the so-called chain reaction is made slower and is finally interrupted.

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According to the present invention the preferred extinguishing medium consists essentially of the following composition:

a) from 10 to 80% by weight of at least one pulverulent, hydrogel-forming polymer, and

b) up to 80% by weight of at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure.

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The preferred polymers used for mixing purposes are crosslinked polymers forming hydrogels produced by the polymerization of acrylamide and/or acrylic acid and/or a salt thereof in the presence of up to 2% by weight of bisacrylamidoacetic acid, trimethylol propane triacrylate and/or tetraallyloxyethane.

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The substances used for mixing purposes have a large surface structure and/or a capillary and/or fibrous structure and are preferably used individually or in mixtures and are selected from the group kieselguhr, sawdust, paper fibres, fibrous or ground cellulose, fibrous or ground plastics, ground foamed plastics and amorphous hydrophobic silicon dioxide.

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The use of an adhesive, which is preferably organic based, e.g. wallpaper pastes, is intended to improve the adhesion of the extinguishing medium to solid surfaces in wet extinguishing media. Up to 30%, and desirably up to 10%, by weight is preferably used.

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The use of a wetting agent, e.g. of an organic biodegradable base, reduces the surface tension of the water, so that the flowability in the capillaries or fibres is improved. Up to 10%, and desirably up to 5%, by weight is preferably used.

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The use of a dye in the extinguishing medium, e.g. of a biodegradable base, offers the advantage that it is possible to visually detect whether and where extinguishing

media have already been used. Up to 5%, and desirably up to 1%, by weight is preferably used.

A flow accelerator, e.g. of a polymer base, reduces the flow resistance in pipelines and hoses. Up to 10%, and desirably up to 5%, by weight is preferably used.

When storing wet extinguishing media in containers or the like over long periods of time, a stabilizer, e.g. in the form of a disinfectant, such as hydrogen peroxide, will prevent water putrefaction. Up to 10%, and desirably up to 0.3%, by weight is preferably used.

The preparation and composition of the extinguishing medium according to the invention are described in greater detail hereinafter with reference to Examples 1 to 14.

Example 1

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In a container well insulated by foamed plastics material 20 are placed 635 g of water at ambient temperature and 180 g of sodium hydrogen carbonate and 240 g of acrylic acid are dosed in such a way that a foaming over of the reaction solution is avoided and the latter is cooled to a temperature of 10 to 8°C. This is followed by the addition 25 of 1.5 g of sodium diisooctyl sulphosuccinate and a solution of 2 g of Genapol OX 130 (Genapol = trade mark of Farbwercke Hoechst AG for washing, wetting and dispersing agents based on alkyl polyglycol ethers and ethylene oxidepropylene oxide block polymers) and 2.5 g of 1,1,1-30 trimethylol propane triacrylate as crosslinking agents. At a temperature of 8 to 10°C there is a successive introduction and stirring in of, the initiators, a redox system consisting of 2.0 g of 2,2'-azobisamidinopropane dihydrochloride, dissolved in 2.5 g of water, 0.6 g of 35

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pctassium peroxodisulphate, dissolved in 20 g of water, and 0.05 g of ascorbic acid, dissolved in 10 g of water. The reaction solution was left to stand without stirring and 23 a result of the commencing polymerization the temperature rose to 80°C and a solid gel was obtained.

Example 2

In a container well insulated by foamed plastics material were placed 635 g of water at ambient temperature and 180 g of sodium hydrogen carbonate and 240 g of acrylic acid were dosed in such a way that a foaming over of the reaction solution was avoided and the latter was cooled to This was followed by the a temperature of 10 to 8ºC. addition of 1.5 g of sodium diisooctyl sulphosuccinate and 2 g of Genapol OX 130. At a temperature of 8 to 10°C the initiators, a redox system, consisting of 0.2 g of 2,2'azobisamidinopropane dihydrochloride, dissolved in 2.5 g of water, 0.6 g of potassium peroxodisulphate, dissolved in 20 g of water, and 0.05 g of ascorbic acid, dissolved in 10 g of water, were successively added and well stored. reaction solution was left to stand without stirring and as a result of the commencing polymerization the temperature rose to 80°C and a solid gel formed.

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Example 3

1000 g of the polymer gel obtained according to Examples 1 or 2 were mechanically comminuted, mixed with 300 g of kieselguhr and 20 g of sodium silicate and/or potassium silicate and/or ammonium polyphosphate as flameproofing agents in 30% solution in water, homogeneously kneaded in a kneader, dried at temperatures above 80%C and ground to a powder.

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Example 4

2500 g of the product according to Example 1 or 2 was mixed after polymerization with 10 g of ammonium polyphosphate in 30% solution in water and 400 g of kieselguhr, homogeneously kneaded in a kneader, dried at temperatures above 80°C and ground.

Example 5

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2000 g of the product according to Example 1 or 2 were mixed after polymerization with 5 g of a 25% aqueous sodium silicate solution and 400 g of kieselguhr, homogeneously kneaded in a kneader, dried at temperatures above 80°C and ground.

Example 6

4000 g of the product according to Example 1 or 2 were
mixed after polymerization with 10 g of a 30% aqueous
potassium silicate solution and 500 g of kieselguhr,
homogeneously kneaded in a kneader, dried at temperatures
above 80°C and ground.

25 Example 7

3500 g of the product according to Example 1 or 2 was mixed after polymerization with 20 g of polyethylene glycol and 200 g of kieselguhr, homogeneously kneaded in a kneader, dried at temperatures above 80°C and ground.

Example 8

The solid gel obtained according to Example 1 was mechanically comminuted and then dried at 80°C, followed by comminution to a homogeneous powder, which, in accordance with the designation normally used for such crosslinked hydrogel-forming polymers, is a superabsorber.

Example 9

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40 g of kieselguhr were placed in a mixer and mixed with 0.05 g of a hydrosoluble dye, then mixed with 3 g of polyethylene glycol and mixed to complete homogeneity, followed by mixing with 4 g of a 30% aqueous sodium and/or potassium silicate solution, followed by mixing with 47 g of superabsorber according to Example 8 or some other commercial superabsorber up to homogeneity.

Example 10

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40 g of kieselguhr were placed in a mixer and mixed with 0.05 g of a hydrosoluble dye, then mixed with 2 g of polyethylene glycol and up to complete homogeneity, followed by mixing with 3 g of a 30% aqueous ammonium polyphosphate solution and then with 50 g of a superabsorber according to Example 8 or some other commercial superabsorber up to homogeneity.

Example 11

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30 g of cellulose were placed in a mixer and mixed with 0.05 g of a hydrosoluble dye, followed by mixing with 15 g of a 30% aqueous solution of sodium silicate and/or potassium silicate and/or ammonium polyphosphate and 5 g of polyethylene glycol up to complete homogeneity, followed by

mixing with 55 g of superabsorber according to Example 8 up to homogeneity.

Example 12

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40 g of cellulose were placed in a mixer, mixed with 0.05 g of a hydrosoluble dye, then with 10 g of a 25% aqueous solution of sodium silicate and/or potassium silicate and/or ammonium polyphosphate and with 3 g of polyethylene glycol up to complete homogeneity, followed by mixing to homogeneity with 80 g of superabsorber according to Example 8.

Example 13

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In a container well insulated by foamed plastics material were placed 635 g of water at ambient temperature and 9 g of sodium silicate and/or potassium silicate and/or ammonium polyphosphate and 180 g of sodium hydrogen carbonate and 240 g of acrylic acid were dosed in such a way that a foaming over of the reaction solution was avoided and the latter was cooled to a temperature of 10 to 8ºC. This was followed by the addition of 1.5 g of sodium diisooctyl sulphosuccinate and a solution of 2 g of Genapol OX 130 and 2.5 g of 1,1,1-trimethylol propane triacrylate. At a temperature of 8 to 10°C the initiators, a redox system, consisting of 0.2 g of 2,2'-azobisamidinopropane dihydrochloride, dissolved in 2.5 g of water, 0.6 g of potassium peroxodisulphate, dissolved in 20 g of water, and 0.05 g of ascorbic acid, dissolved in 10 g of water, were successively added and well stirred. The reaction solution was left to stand without stirring and as a result of the commencing polymerization the temperature rose to 80°C and a solid gel was formed.

Example 14

4000 g of the polymer gel obtained according to Example 13 were mechanically comminuted, mixed with 400 g of kieselguhr, homogeneously kneaded in a kneader, dried at temperatures above 80°C and ground to a powder.

The powder mixtures obtained according to the above Examples were usable with excellent activity as dry extinguishing media or as an extinguishing medium additive to water. In water the powder mixtures had a good swelling behaviour and could be perfectly homogenized without agglomeration. In order to be able to use powder mixtures with flammable constituents without any dust explosion risk as dry extinguishing agents, it is necessary to add fireproofing agents, as indicated in certain Examples.

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CLAIMS

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

- 1. An extinguishing medium for use both as a dry extinguishing medium and as an extinguishing medium additive for addition to water comprising the following constituents:
- a) at least one pulverulent, hydrogel-forming polymer,
 and
- b) at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure,

which are homogeneously mixed to form a free-flowing medium.

- 2. An extinguishing medium according to claim 1, consisting essentially of the following composition:
- a) from 10 to 80% by weight of at least one pulverulent, hydrogel-forming polymer, and
- b) up to 80% by weight of at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure.
- 3. An extinguishing medium according to claim 1 wherein an additive selected from the group consisting of a flame retardant and a fireproofing agent is admixed therewith.
- 4. An extinguishing medium according to claim 1 containing up to 10% by weight of an additive selected from the group consisting of a fire retardant and a fireproofing agent.

5. An extinguishing medium according to claim 1 wherein the at least one polymer used for mixing purposes is a crosslinked hydrogel-forming polymer, produced by the polymerization of a monomer selected from the group consisting of an acrylamide, acrylic acid, a salt of an acrylamide and a salt of acrylic acid in the presence of up to 2% by weight of a crosslinking agent selected from the group consisting of bisacrylamidoacetic acid, trimethylol propane triacrylate and tetraallyloxyethane.

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- 6. An extinguishing medium according to claim 1 wherein the said at least one constituent substance is selected from the group consisting of kieselguhr, sawdust, paper fibres, fibrous cellulose, ground cellulose, fibrous plastics, ground plastics, ground foamed plastics and amorphous hydrophobic silicon dioxide.
 - 7. An extinguishing medium according to claim 1 containing up to 30%, and preferably up to 10%, by weight of a polyglycol.
 - 8. An extinguishing medium according to claim 1 containing up to 30%, and preferably up to 10%, by weight of an organic based adhesive.
 - 9. An extinguishing medium according to claim 1 containing up to 10%, and preferably up to 5%, by weight of a wetting agent having an organic biodegradable base.
 - 30 10. An extinguishing medium according to claim 1 containing up to 5%, and preferably up to 1%, by weight of a dye with a biodegradable base.

- 11. An extinguishing medium according to claim 1 containing up to 10%, and preferably up to 5%, by weight of a polymer-based flow accelerator.
- 12. An extinguishing medium according to claim 1 containing up to 10%, and preferably up to 0.3%, by weight of a stabilizer.

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- 13. A process for producing an extinguishing medium for use both as a dry extinguishing medium and as an extinguishing medium additive for addition to water, comprising the following main constituents:
 - a) at least one pulverulent superabsorber, and
- b) at least one substance with a property selected

 from the group consisting of a large surface structure, a

 capillary structure and a fibrous structure,

which process comprises mixing the said at least one constituent substance, optionally with at least one additive, and simultaneously or subsequently admixing therewith the superabsorber which has been mechanically comminuted and dried and thereby rendered free-flowing.

- 14. A process for producing an extinguishing medium for use both as a dry extinguishing medium and as an extinguishing medium additive for addition to water, comprising the following main constituents:
 - a) at least one pulverulent superabsorber, and
- b) at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure,

which process comprises mixing the said at least one constituent substance with the mechanically comminuted, aqueous superabsorber raw product which has been obtained

by gel polymerization, prior to the drying thereof, and kneading the mixture, followed by drying, grinding and then optionally admixing at least one further constituent.

- 15. A process for producing an extinguishing medium for use both as a dry extinguishing medium and as an extinguishing medium additive for addition to water, comprising the following main constituents:
 - a) at least one pulverulent superabsorber, and
- b) at least one substance with a property selected from the group consisting of a large surface structure, a capillary structure and a fibrous structure,
- which process comprises mixing the said at least one constituent substance with a monomer solution of the superabsorber, polymerizing the mixture obtained according to known gel polymerization techniques, drying and grinding the resulting product and then optionally admixing at least one further constituent.
- 16. A process according to claim 15 wherein an additive selected from the group consisting of a fireproofing agent and a flame retardant is admixed with the monomer solution of the superabsorber.
 - 17. The use of the free-flowing extinguishing medium according to claim 1 as a pulverulent extinguishing medium to be brought to the centre of the fire.
- 18. The use of the free-flowing extinguishing medium according to claim 1 as a wet extinguishing medium swollen to a gel-like consistency by mixing with water and to be brought to the centre of the fire.

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19. The use of the free-flowing extinguishing medium according to claim 1 as a dry extinguishing medium in commercial fire extinguishers and stationary systems.

20. The use of the free-flowing extinguishing medium according to claim 1 as an extinguishing medium additive in extinguishing medium tanks in a useable form selected from the group consisting of a dry form and gel form for use according to fire fighting methods.

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